A role of the membrane|solution interface in electron transfer at self-assembled monolayer modified electrodes

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ABSTRACT

A quinone derivative XQ (= ubiquinone-10 or vitamin K_1) was incorporated into alkanethiol self-assembled monolayers (SAMs) formed on a gold electrode and the effect of the SAM|solution interface on the electron-transfer kinetics of XQ was investigated by cyclic voltammetry. It was confirmed that when a longer alkanethiol (e.g., 1-octadecylmercaptan) was used to form the SAM, the redox reactions of XQ were slowed significantly not only by the separation of XQ from the Au|SAM interface but also by the inhibition of the electron-transfer-coupled proton transfer across the SAM|solution interface. When a strongly hydrophobic supporting-electrolyte cation such as tetrabutylammonium or tetrapentylammonium was added to the aqueous solution, however, the redox reaction of XQ at the SAM modified electrode became faster. In order to explain this reason, we have proposed a model in which the adsorption of strongly hydrophobic cations on the SAM|solution interface induces a structural disorder of the monolayer and then facilitates the supply of protons from the solution to XQ in the monolayer. An evidence of the adsorption of the strongly hydrophobic cations on the SAM|solution interface was obtained from the measurements of the double-layer capacitance of the SAM modified electrode by alternating-current voltammetry.

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1. Introduction

It is well known that the charge (ion and/or electron) transfer reactions occurring in biomembranes are keys in energy production in the mitochondrial respiratory chain system and signal transaction in neural systems [1]. The Galvani potential difference across a biomembrane may play important roles in the charge transfer processes, however the detailed mechanisms have not fully been clarified. For this perspective, several biomembrane models have been used, including bilayer lipid membranes [2,3] and polarized oil|water (O|W) interfaces [4–6]. A variety of ion or electron transfers occurring at the biomembrane models have been studied by electrochemical techniques. Although the lipid membrane is one of the most similar model to real biomembranes, however it comprises two membrane|solution interfaces whose Galvani potential differences cannot be controlled (or measured) independently. On the other hand, the O|W interface or the interface between two immiscible electrolyte solutions (ITIES) comprises only a single interface whose Galvani potential difference can be controlled potentiostatically [4,7–9]. However, the bulk oil

phase may be somewhat different from the thin lipid bilayer in biomembranes.

As another prospective biomembrane model, the self-assembled monolayer (SAM) has been used, which being an oriented monolayer film formed by spontaneous chemisorption of organic molecules such as thiols on a solid surface (typically, a gold electrode surface [10–13]). Electrochemical behaviors of ubiquinone-10 (UQ) and vitamin K incorporated into alkanethiol SAMs were previously studied by cyclic voltammetry [14]. Immobilization of a redox protein such as cytochrome *c* on a carboxylic acid-terminated SAM was also investigated and the electron transfer kinetics of cytochrome *c* was discussed [15–17]. The ferrocene- and quinone-terminated SAMs have been prepared to study electron transfer processes between the redox moiety and the base metal [18–21]. This application as an electron mediator (e.g., in biosensors) has also been studied [22–26]. Moreover, ion permeability of monolayers and its relationships to the steric structure of monolayers or the size of ions have been studied [27,28]. In these studies, the effects of chemical properties or structures of SAMs on redox processes have mainly been studied based on voltammetric data.

Despite many studies of SAM modified electrodes, there have been few studies focusing on the Galvani potential difference of the SAM|solution interface and its possible role in electrode

processes. Provided the SAM|solution interface is analogous to the O|W interface, its Galvani potential difference should be deeply committed to the charge transfer process at the SAM modified electrode. In this study, we incorporated UQ or vitamin K_1 (VK_1) into alkanethiol SAMs on gold electrodes according to the method proposed by Takehara et al. [14], and then investigated the effects of supporting electrolytes on the electrode reactions. The reduction/oxidation peak potentials of the quinone derivative XQ (= UQ or VK_1) at the SAM modified electrodes were affected by the hydrophobicity of supporting-electrolyte cations, suggesting a plausible role of the Galvani potential difference of the SAM|solution interface. However, further consideration involving the participation of protons in electrode processes and some additional experiments made us to propose another possible mechanism based on the adsorption of supporting-electrolyte cations on the surface of the SAM. The adsorption of a hydrophobic cation causes the structural disorder of the SAM, so that the proton transfer from the solution into the SAM and the succeeding electron transfer are facilitated. In this paper, the validity of this mechanism has been discussed.

2. Experimental

2.1. Reagents

UQ (>98%) was purchased from Sigma–Aldrich and used without further purification. VK_1 was purchased from Kishida Chemical, Japan and used without further purification. 1-Octadecylmercaptan (OM), 1-dodecylmercaptan (DM), 1-heptylmercaptan (HPM), KCl (>99.5%), tetramethylammonium chloride (TMACl; >99.0%), tetraethylammonium chloride (TEACl; >98.0%), tetrapropylammonium chloride (TPrACl; >97.0%), tetrabutylammonium chloride (TBA; >98.0%), and tetrapentylammonium chloride (TPnACl; >98.0%) were purchased from Tokyo Chemical Industry, Japan and used without further purification. 11-Hydroxy-1-undecanethiol (HUT) was purchased from Dojindo Laboratories, Japan and used without further purification. Unless noted otherwise, the pH of the test aqueous solution was adjusted at 7.2 with 0.01 M NaH_2PO_4–Na_2HPO_4 buffer.

2.2. Electrode preparation

The formation of SAM on a gold electrode and the incorporation of XQ therein were performed in a similar manner to that reported previously [14]. A gold disk electrode (purchased from BAS Inc., Japan; 1.6 mm diameter; polycrystalline) was polished with 0.25 μm diamond slurry and rinsed with ethanol and deionized water. Alkanethiol SAMs were formed on the gold-electrode surface by soaking in 10 mM ethanol solutions of OM, DM, and HPM for 30 min, followed by rinsing with ethanol. Also, a similar SAM modified electrode was prepared by using HUT, by soaking the electrode in a 1 mM ethanol solution of HUT for 1 h. The incorporation of XQ into these SAMs was performed by soaking the SAM modified electrodes in a 0.4 mM acetone solution of XQ for 4 min under ultrasonic field.

2.3. Voltammetric measurements

Cyclic voltammetry (CV) and alternating-current voltammetry (ACV) were performed with a conventional three-electrode system and the Hokuto Denko HA1010mM1A potentiostat. A SAM modified gold electrode, a platinum wire electrode, and a Ag/AgCl (saturated KCl) electrode were used as the working, counter, and reference electrodes, respectively. CV and ACV measurements and the data acquisition were carried out by using a laboratory-constructed computer assisted system. In CV measurements, the voltage sweep rate was 0.02–0.1 V s^{-1}. In ACV measurements, a small ac voltage (frequency, f = 50 Hz; 0.010 V rms) was superimposed on a dc voltage sweep at 0.05 V s^{-1}. Real and imaginary components of the ac admittance ($Y = Y' + jY''$, with $j = \sqrt{-1}$) were detected by a lock-in amplifier (NF Co., Japan; LI5640). Using a simple capacitance model, the double-layer capacity (C_{dl}) of the SAM modified electrode was determined from Y'' as $C_{dl} = Y''/(2\pi fA)$ (A, the surface area) and recorded against the dc electrode potential, E vs. Ag/AgCl (saturated KCl). All the voltammetric measurements were performed in an air-conditioned room and the temperature of the electrolytic cell was kept at 25 ± 2 °C.

3. Results and discussion

Fig. 1 represents the cyclic voltammograms of UQ incorporated into SAMs formed on a gold electrode, in which the SAMs being prepared from different alkanethiols, i.e., OM, DM, and HPM. Each voltammogram shows one pair of clear cathodic and anodic peaks due to the redox reactions of UQ, as reported by Takehara et al. [14]. It should here be noted that the cathodic and anodic peaks were widely separated, suggesting a strong inhibitory effect of the SAMs on the redox reactions of UQ. As seen in Fig. 1, this effect is increased with increasing the carbon number of the alkanethiols in the order of HPM (7) < DM (12) < OM (18). A possible cause of the large peak separation showing a slow electron-transfer rate is the separate location of the redox species (i.e., UQ) from the gold electrode surface. It is well known that the electron-transfer rate is extremely dependent on the distance from the electrode surface to the redox species, being exponentially decreasing as the distance increases [7]. In contrast to the UQ incorporated into SAMs, the UQ directly adsorbed on the surface of a mercury electrode shows a reversible cyclic voltammogram, which suggests a fast electron transfer reaction [29]. On the other hand, UQ molecules in the present SAMs probably exist more or less separately from the electrode surface. This would decrease the electron-transfer rate with increasing the distance. It seems unlikely that the UQ molecules are mostly located in pinholes of the SAM, because if so, they could come closer to the electrode surface and would facilitate the electron transfer of UQ (and concurrent proton transfer via pinholes), giving a more reversible voltammogram with a narrower peak separation.

In this study, we first focused another possible effect on the large peak separation, i.e., the effect of the Galvani potential difference ($\Delta_s^{SAM}\phi$) across the SAM|solution (= s) interface. If the SAM|solution interface behaves in a similar fashion to an O|W interface, a considerable contribution from $\Delta_s^{SAM}\phi$ to the electrode potential ($\Delta_s^{Au}\phi$) is expected; note that $\Delta_s^{Au}\phi = \Delta_{SAM}^{Au}\phi + \Delta\phi_{SAM} + \Delta_s^{SAM}\phi$, where $\Delta_{SAM}^{Au}\phi$ and $\Delta\phi_{SAM}$ are the Galvani potential difference across the Au|SAM interface and the potential difference occurring within the SAM, respectively; for the potential distribution on the electrode surface, see Fig. S1 (Supplementary material). It would also be possible to change the contribution of $\Delta_s^{SAM}\phi$ by controlling the distribution of ions between the SAM and solution phases. Then, we have examined the effect of supporting electrolyte on the cyclic voltammogram of UQ incorporated into SAMs. Fig. 2 displays the cyclic voltammograms recorded at the OM SAM-modified gold electrode, which was immersed in aqueous solutions of 0.1 M KCl, TMACl, TEACl, TPrACl, TBACl, and TPnACl (pH 7.2). A clear tendency was observed for the cathodic and anodic peak potentials (E_{pc} and E_{pa}) to shift to more positive and negative values, respectively, with increasing the hydrophobicity of the electrolyte cation. In Fig. 3, the E_{pc} observed for the OM, DM, and HPM SAM-modified electrodes is